

# Closed-shell interaction in silver and gold chlorides

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Hartree-Fock and coupled-cluster calculations have been performed for cubic AgCl and for AuCl having a cubic or the observed structure with space group  $I4_1/amd$ . Cohesive energies and lattice constants are in excellent agreement with experiment for AgCl; for AuCl we find good agreement, and the experimental structure is correctly predicted to be lower in energy than the cubic one. Electron-correlation effects on lattice constants are very large, of up to 0.8 Å for cubic AuCl. We especially discuss the strength of the closed-shell interactions, and for the first time a quantitative analysis of the so-called "aurophilic" Au(I)-Au(I) interaction is presented in solids.

## I. INTRODUCTION

In recent years, the rôle of attractive closed-shell interactions in inorganic chemistry has been intensively investigated<sup>1</sup> and the results have been summarized in several review articles<sup>2,3</sup>. Both structural, spectroscopic, and energetic evidence exist. The structures exhibit short secondary M-M distances (M = Cu(I), Ag(I), Au(I), Tl(I), etc.) and inwards bending of the primary L-M-L' bonds. The spectroscopic evidence incorporates Raman frequencies of the M-M stretching mode. The interaction energies can be directly measured as activation energies by temperature-dependent NMR and from optically monitored chemical equilibria.

*Ab-initio* theoretical studies exist for intramolecular interactions and for dimers. They invariably yield repulsive interactions at Hartree-Fock level and reproduce the attraction at correlated level. Relativistic effects enhance the interaction for gold<sup>4</sup>. It should be added that the free (Au<sup>+</sup>)<sub>2</sub> dimer remains repulsive<sup>5</sup>. In this sense the ligands are essential.

In this article, we investigate these interactions for the first time in a solid, using quantum-chemical *ab-initio* methods (Hartree-Fock in combination with the coupled-cluster approach). We consider the systems AgCl and AuCl. While the former has rocksalt structure, the latter one exhibits a rather complicated tetragonal structure, with space group  $I4_1/amd$ <sup>6</sup>, which is thermodynamically stable in a region between  $\sim 90^\circ\text{C}$  and  $342^\circ\text{C}$ <sup>7</sup>. This is

just an example of a system with relatively short Au-Au distances. For the sake of comparison, we performed calculations for both the cubic and the experimental structure, in the case of AuCl.

## II. THE METHOD

The calculations consist of two parts. First, Hartree-Fock (HF) calculations on the solid are performed with the program package CRYSTAL<sup>8-10</sup>. After that, electron correlation for the extended systems is included by means of a Bethe-Goldstone-like expansion, in terms of correlation contributions from localized orbital groups ("method of local increments"<sup>11</sup>). In a series of studies<sup>11-14</sup>, it has been shown that this method is capable of yielding results of high quality. For a detailed account of the method as applied to ionic compounds, see Refs. 13,14. (In Ref. 14, we also showed how to determine van der Waals  $C_6$  parameters with this method.) It should be mentioned that we determined individual increments in finite model systems (embedded clusters), using an ionic embedding, with cationic pseudopotentials in the first sphere and point charges beyond. Such an embedding was applied to all systems considered in the present paper, including AuCl in the experimental structure (which is not fully ionic, cf. below). In order to check the validity of our description, we compared the increments taken from different clusters (with two or three explicitly described ions) and various representations of the Madelung field. The experimental structure turned out to be more sensitive with respect to the number of point charges than the rocksalt structure, so that a larger number is necessary in the former case. However, the results with  $8 \times 8 \times 8$  unit cells were nearly identical (up to a few  $\mu\text{H}$ ) to those of calculations where only  $6 \times 6 \times 6$  unit cells were represented by point charges, which ensures convergence of the results with the larger set. A more severe problem was the transferability of the increments which was less good in the observed AuCl structure than in the cubic one. As correlation scheme, we chose the (size-consistent) coupled-cluster approach with single and double substitutions (CCSD), and the CCSD(T) scheme including triples by perturbation theory.

For Ag and Au, we used energy-consistent relativis-

tic 19-valence-electron pseudopotentials<sup>15</sup>, in combination with the corresponding optimized ( $8s7p6d$ ) valence basis sets (uncontracted) and augmented with  $3f$  and  $2g$  functions (Ag  $f/g$ -exponents are 2.54, 0.73, 0.20 / 1.58, 0.50; Au  $f/g$ -exponents are 1.41, 0.47, 0.15 / 1.20, 0.40). Results for the neutral atoms and singly charged cations, with these pseudopotentials and basis sets, are shown in Table I; the ionization potentials turn out to be in good agreement with experiment. For Cl, an all-electron description was chosen; the basis set used for the correlation calculations is a  $[6s5p3d2f]$  augmented valence triple zeta basis set<sup>16</sup> already employed in earlier calculations on alkali halides<sup>14</sup>. Finally, single-valence-electron pseudopotentials<sup>17</sup> for Ag and Au were used as part of the embedding, in our calculations, in order to model the cage effect on the explicitly described cluster atoms (especially the anions).

In the Hartree-Fock calculations,  $f$  and  $g$  polarization functions as well as very diffuse functions had to be omitted for Ag and Au. The outermost  $spd$  exponents were reoptimized for the solid. (In the case of AuCl, two different basis sets were optimized for the two different crystal structures, respectively.) The Cl basis set was taken from Ref. 19, again reoptimizing the diffuse exponents. The basis sets for the Hartree-Fock calculations are given in Table II.

### III. HARTREE-FOCK CALCULATIONS

As mentioned, HF self-consistent field (SCF) calculations were performed with the program package CRYSTAL (Ref. 8). Results, together with those of the next section, are summarized in Table III. For AgCl, the SCF cohesive energy,  $E_{coh}$ , is too small by 30% with respect to experiment. This, of course, reflects the well-known SCF error for bond-breaking. The situation is significantly improved for the lattice energy,  $E_{lat}$ , i.e. the energy for separating the crystal into  $Ag^+$  and  $Cl^-$  ions — however, experiment is still underestimated by 20%. This has to be contrasted with the situation for the alkali halide crystal NaCl, which has a SCF lattice constant comparable to AgCl: the percentage of the SCF errors for both  $E_{coh}$  and  $E_{lat}$  are smaller by roughly 10-15%<sup>14,19</sup>. This should not be taken as an indication of increased covalent contributions in AgCl — the Mulliken population analysis shows a still nearly perfect ionic behaviour, with charges of  $\pm 0.9 e$  for Ag and Cl. However, it is certainly an indication that the correlation contribution of the  $Ag^+$  core is much more important than for the alkali halides. A similar conclusion can be drawn from considering the lattice constant: for AgCl, SCF yields a deviation from experiment of  $0.5 \text{ \AA}$  (9%) — in contrast to 'normal' quantum-chemical SCF results for covalent systems, it is an overestimation. This points to the importance of bond-shortening correlation effects like dynamic polarization and dispersion in AgCl. Of course, these effects

are also acting in the alkali halides, but their magnitude is significantly smaller (3.5% in NaCl). Note that this is in line with the trend of the 'in-crystal' polarizabilities of the cations  $Na^+$  and  $Ag^+$  to be discussed below. The SCF bulk modulus of AgCl ( $\sim 23 \text{ GPa}$ ) grossly underestimates experiment, by more than 50%.

Calculations for AuCl in the cubic rocksalt structure yield a SCF lattice constant and a SCF lattice energy both very similar to the corresponding values for AgCl. Also, according to our population analysis, the charges in AuCl are  $\pm 0.9 e$ , i.e. essentially the same as in AgCl. Thus, it may be concluded that the closed-shell repulsive potentials are quite similar for the (relativistic)  $Ag^+$  and  $Au^+$  ions. The cohesive energy of AuCl, on the other hand, is smaller by more than 1 eV than in AgCl. This can be explained by the relativistic stabilization of the  $6s$  electron in the free Au atom<sup>18</sup>. Turning now to our results for the experimental tetragonal ( $I4_1/amd$ ) structure of AuCl, we find it to be energetically nearly degenerate to the cubic structure, at the SCF level, with the latter very slightly lower (by  $\sim 1 \text{ mH}$ ). However, one can not conclude that at the Hartree-Fock limit (i.e. with a complete basis set) the experimental structure would still be higher in energy. In the rocksalt structure, the  $d$ -occupancy on the chlorine atom is only 0.01  $e$  and omitting the  $d$ -function decreases the cohesive energy by only 2 mH, whereas the  $d$ -population in the experimental structure is 0.05  $e$  and the energy decreases by 17 mH without this function. This results from the fact that a static  $d$ -polarization is symmetry-forbidden in the rocksalt structure<sup>19</sup>. Thus, one might expect that additional polarization functions (e.g.  $f$  functions on Au) should further lower the energy of the experimental structure compared to the cubic one, and then already at the HF limit the experimentally observed structure would become more stable. As already indicated by the stronger static polarization effects, we find a tendency towards more covalent bonding in the experimental structure: this shows up in the Mulliken population analysis, where the charge transfer  $Au \rightarrow Cl$  is found to be not more than 0.5  $e$ . In line with this change in bonding, the SCF overestimation of the lattice constant (5.8% for the experimental structure) is smaller than for the cubic one. (Note, at this point, that we performed only calculations for the isotropically expanded experimental structure, i.e. the ratio  $\frac{a}{c}$  was kept fixed as well as the parameter  $z = 0.19$  which characterizes the  $z$ -component of the chlorine atoms with respect to the gold atoms.)

For AgCl, Hartree-Fock and density functional calculations have been performed<sup>20,21</sup>. The Hartree-Fock results are similar to ours (i.e. about 70 % of the cohesive energy is recovered and the lattice constant is overestimated by  $0.4\text{-}0.5 \text{ \AA}$ ). In Ref. 21, a detailed analysis of relativistic contributions was made, and reductions of the bond length, of about 1 %, and of the cohesive energy, of about 15 mH, were found when effects of relativity were included. Correlation-energy density-functional corrections improve the HF results significantly; however,

the lattice constant is still overestimated<sup>20</sup>. An *ab-initio* treatment of electron correlation in silver and gold halides has not been attempted so far.

#### IV. CORRELATION CALCULATIONS

The calculations were done with the program package MOLPRO<sup>22,23</sup>. The correlated orbitals are  $3s$  and  $3p$  for Cl; for Ag and Au we correlated the highest occupied  $d$ -shell (i.e.  $4d$  for Ag,  $5d$  for Au). We found in CCSD calculations for AgCl that additionally correlating the inner-core  $4s$  and  $4p$  orbitals only slightly changes the results (e.g., the Ag-Cl increment for next neighbors changes from 0.008077 H to 0.008576 H). The incremental expansion is made in terms of localized orbital groups which can be attributed either to the metal cations,  $M^+$ , or are mainly centered on the chlorine anions. However, this does not imply any *a priori* assumption with regard to the ionicity of the system.

In Tables IV and V, we give results for AgCl and AuCl (cubic structure) at two different lattice constants; corresponding results for the tetragonal structure of AuCl are contained in Table VI. Let us first consider the intra-ionic 'one-body' contributions which are obtained when correlating only one embedded ion. As can be seen from the Tables, these energies are not too different from those of the free ions and therefore make only a minor contribution to the lattice energy. Much more important are the van der Waals like inter-ionic two-body contributions; these are determined by correlating a pair of ions and subtracting off the corresponding intra-ionic one-body terms. We begin the discussion with results for the rocksalt structure. The dominant two-body contributions clearly are the metal-chlorine terms. This is to be expected since these ions are nearest neighbors and the polarizability is not only high for the  $Cl^-$  ions but also for the metal ions due to their large number of electrons and large ionic radii. The chlorine-chlorine contributions are smaller by a factor of 4 ... 5 because of the larger distance between nearest-neighbor Cl ions in the lattice, but in turn are still significantly more important (by a factor of 3 ... 4) than the metal-metal ones. It may be interesting to compare the AgCl correlation-energy increments to those of NaCl which has about the same lattice constant. There, the Cl-Cl increments are the dominant ones, with the Na-Cl terms smaller by  $\sim 20\%$  and the Na-Na ones completely negligible — of course, this just reflects the relation between the metal-ion dipole polarizabilities  $\alpha$ : that of  $Ag^+$  being only a factor 2 smaller than for  $Cl^-$ ,  $\alpha(Na^+)$ , on the other hand, being smaller than  $\alpha(Cl^-)$  by more than an order of magnitude. It has been argued<sup>24</sup> that the difference in the strength of van der Waals interactions is responsible for the unusual features in the cohesive properties of AgCl as compared to the alkali halides. In fact, according to our present CCSD(T) calculations (and those of Ref. 14), the ratio of inter-

ionic correlation contributions in AgCl and NaCl, at the equilibrium lattice constants, is  $\sim 4.4$ , which is not very different from the ratio of  $\sim 6$  estimated by Bucher<sup>24</sup> on the basis of a semiempirical fit to solid-state data. Comparing now inter-ionic correlation in AgCl and AuCl, one notes an increase  $AgCl \rightarrow AuCl$  by about a factor 2. Of course, this has to do with the increase of the metal  $\alpha$  but, as shown by the increase of the Cl-Cl increments, is also influenced by the reduction of the lattice constant in AuCl. In spite of the increased importance of inter-ionic van der Waals interaction in AuCl, the Au-Au increments are still rather small in absolute value: for a given Au-Au pair of nearest neighbors, the effect is only  $\sim 0.04$  eV. Let us now consider the experimental tetragonal AuCl structure. Here, distances between the ions are shorter, with a lower coordination number, however (smaller weight factors). This means that, for example, the Au-Cl two-body increment for next neighbors is much larger than in the rocksalt structure, but has to be multiplied with a weight factor of two only (six in the cubic structure). The sum is still clearly dominated by the Au-Cl contributions which in total are roughly the same (within  $\sim 15\%$ ) as in the cubic structure, the same holds for the Cl-Cl increments. In contrast to that, the correlation contribution between Au ions increases by a factor of  $\sim 3$ . The largest van der Waals attraction between an individual Au-Au pair (or, to be more precise, between the two  $d^{10}$  shells) is now  $\sim 0.2$  eV, i.e. relatively strong (comparable to the values given in Figure 36 of Ref. 3 at this distance of 3.2 Å). However, this attraction alone would certainly not be strong enough to overcompensate the electrostatic repulsion of the positively charged ions (even if a reduced charge of 0.5  $e$ , according to the Mulliken population analysis, is assumed). We have no indication, furthermore, for an additional stabilizing covalent interaction between the Au ions: the SCF overlap population is -0.02. On the other hand, the  $6s$ -like valence population on Au could give rise to non-negligible valence (and core-valence) correlation contributions — only, we cannot separate these contributions from those of the Cl ions, since they cannot be attributed to different localized orbitals.

In Table VII, we display 'in-crystal' ionization potentials (IP), dipole polarizabilities ( $\alpha$ ) and  $C_6$  coefficients for the cubic structures. The IP and  $\alpha$  were calculated for an embedded single ion (treated with high-quality basis set and surrounded by pseudopotentials/point charges). For evaluating  $C_6$ , we multiplied individual 2-body increments, for a given species, involving ions with the smallest internuclear distance in the lattice, by the sixth power of their distance. Of course, this implies the assumption of a pure van der Waals interaction between these ions, which is certainly only approximately satisfied. As already mentioned, the in-crystal polarizability of Ag is larger by a factor  $\sim 10$  than that of Na, i.e. essentially comparable to Rb<sup>14</sup>, and the  $\alpha$  value of Au is even higher by a factor  $\sim 1.5$ . The  $C_6$  coefficients for Cl-Cl in AgCl, and even more so in AuCl, are larger than for the alkali

halides<sup>14</sup>. While this trend can be qualitatively explained for AgCl using the London formula, cf. Table VII, the rationalization for AuCl is more difficult. Apparently, the spill-over of charge on neighboring crystal ions is larger in AuCl, and the interaction is less van der Waals-like. The  $C_6$  coefficients for metal-chlorine interaction are next highest in magnitude. That of AgCl is in good agreement with RbCl, as expected from the similarity of the polarizabilities, and the change from AgCl to AuCl roughly scales with the metal polarizabilities again. Turning now to the interactions between metal ions: our CCSD  $C_6$  value for Ag-Ag (71 a.u.) is in the range of 62 to 375 a.u. given in Ref. 25. The Au-Au  $C_6$  coefficient (149 a.u.) is certainly very high compared to other metal-metal coefficients because of the high polarizability, but still significantly lower than both Au-Cl and Cl-Cl. This coefficient is also much lower when comparing to results from literature for  $C_6$  coefficients characterizing the van der Waals interaction between two molecules, for example for the dimer  $(\text{H}_3\text{P-Au-Cl})_2$  a long-distance  $C_6$  limiting value of 1830 a.u. has been calculated<sup>4</sup>.

In order to check whether or not intra-ionic and 2-body inter-ionic correlation-energy increments give a reliable account of correlation effects in the systems considered, we also calculated several three-body increments. They were determined, as non-additivity corrections, in (embedded) clusters with three explicitly correlated ions, cf. footnotes to Tables IV, V, and VI. As in earlier work they do not make an important contribution to the total energy. This does not seem to support the argument of Ref. 24 that three-body van der Waals interactions are important in AgCl. However, it is not clear whether the violation of the Cauchy relation of the elastic constants in AgCl would show up explicitly by means of 3-body increments in our formalism, or rather by an (angular) dependence of the 2-body ones on changes of lattice geometry.

Our final results are obtained by adding the (weighted) sum over all correlation-energy increments to the SCF energies. By doing this for a range of lattice constants, we can monitor the influence of correlation on lattice constants and bulk moduli (see Table III). While HF cohesive energies underestimate the experimental values by 30 % (AgCl) or 50 % (AuCl), the agreement is excellent at the correlated level for AgCl with deviations of less than 2%. For AuCl, we find a less good agreement with an overestimation of 34 mH (17 %) for the cohesive energy or 30 mH (7%) for the lattice energy. Lattice constants are strongly reduced due to the van der Waals interaction, by up to 0.8 Å or 14 % (CCSD(T)) in the hypothetical cubic structure of AuCl. In the rocksalt structure, AuCl would have a shorter lattice constant (by 0.3 Å) than AgCl. The shortest Au-Cl distances found in the tetragonal structure of AuCl are 2.36 Å, the shortest Au-Au and Cl-Cl distances are 3.22 Å and 3.21 Å, respectively (our calculated CCSD(T) values are 3.9 % shorter). The reduction of the distances compared to the cubic structure (CCSD(T) values: Au-Au = Cl-Cl

= 3.69 Å, Au-Cl = 2.61 Å) may be explained with the reduced ionic radii in systems with smaller coordination number<sup>26</sup>. The larger deviation of our results for the experimental tetragonal AuCl structure as compared to the cubic AgCl one is probably due to the less good transferability of the increments in the former structure (see footnotes to Tables IV, V, and VI). When we extract the largest Au-Cl increment (which makes the most important correlation contribution to the lattice energy) from a cluster with three (instead of two) explicitly described ions, the cohesive energy is reduced by 12.5 mH and the deviation of the lattice constant from experiment shrinks to 3.5 %, at the CCSD(T) level. Note also that our calculations refer to zero temperature where AuCl is experimentally unstable. While the cubic structure for AuCl was slightly lower in energy (by 1 mH) than the experimental one, at the SCF level, the situation is reversed by correlation, and the experimental structure is calculated to be significantly more stable now (by 39 mH). About half of the stabilization is due to  $\text{Au}^+\text{-Cl}^-$  pairs, the next important contribution ( $\sim 40\%$ ) coming from the van der Waals interaction of the  $\text{Au}^+$  cores. Both effects involve correlation of the Au 5d shell.

## V. CONCLUSION

We have extended the method of local increments to 4d and 5d transition-metal compounds. The results for cohesive energy and geometry are in excellent agreement with experiment for AgCl and in good agreement for AuCl. For AuCl, we find the experimental structure with space group  $I4_1/amd$  to be lower in energy by  $\sim 39$  mH than the hypothetical rocksalt structure. While the latter structure corresponds to nearly purely ionic bonding, the experimental structure features significant covalent bonding. The largest correlation contributions to the lattice energy come from pairs of nearest-neighbor metal/halide ions (up to  $\gtrsim 1$  eV for a Au-Cl pair in the experimental structure of AuCl). However, while the metal-metal pairs give only very small van der Waals-like contributions in the cubic structure of AgCl and AuCl ( $\leq 0.04$  eV for a single M-M interaction), the correlation effect of Au-Au pairs reaches that of the Cl-Cl ones ( $\sim 0.2$  eV per pair) in the tetragonal structure. The stabilization of the tetragonal structure with respect to the cubic one is essentially a correlation effect involving excitations from the Au 5d shells. The influence of correlation on the geometry turns out to be very important: the lattice constant is reduced by 9 % for AgCl and 10 % AuCl (experimental structure), for AuCl in the rocksalt structure the reduction would be even larger (14 %).

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TABLE I. The first ionization potential (IP) for Ag and Au is given in Hartrees units, evaluated at Hartree-Fock and correlated levels, in comparison with experimental values.

Atom	RHF	CCSD	CCSD(T)	expt. <sup>27</sup>
Ag	0.233121	0.269033	0.272983	0.27842
Au	0.282265	0.326956	0.331273	0.33904

TABLE II. Exponents and contraction coefficients (in parentheses) of the basis sets for the CRYSTAL calculation. In the case of AuCl, we optimized two different basis sets for the cubic and the experimental structure.

Exponent (contraction) AgCl			Exponent (contraction) AuCl		
			cubic lattice      experimental lattice		
Ag	1s, 2sp, 3spd	pseudopotential <sup>15</sup>	Au	1s, 2sp, 3spd, 4spdf	pseudopotential <sup>15</sup>
	4s	9.0884420 (-1.9648132) 7.5407310 (2.7332194) 2.7940050 (0.1991148)		5s	20.1152990 (-0.1597614) 12.1934770 (0.7893559) 6.0396260 (-1.5714057)
	5s	1.4801580		6s	1.3737210
	6s	0.65		7s	0.65001      0.630
	7s	0.16		8s	0.171      0.102
	4p	4.4512400 (-6.0833780) 3.6752630 (6.4168543)		5p	8.6096650 (2.0982231) 7.3353260 (-3.0458670)
	5p	1.2912880 (0.7539735) 0.6525780 (0.2730597)		6p	1.9129700 (0.3791452) 1.0576950 (0.6456428)
	6p	0.38		7p	0.452      0.442
	4d	7.9947300 (-0.0163876) 2.7847730 (0.2814107) 1.2097440 (0.4863264) 0.5053930 (0.3867258)		5d	4.1439490 (-0.4058458) 3.5682570 (0.4275070) 1.3443240 (0.4755405) 0.5552890 (0.5610972)
	5d	0.198851		6d	0.192      0.188
Cl	1s, 2sp, 3sp	as in Ref. 19	Cl	1s, 2sp, 3sp	as in Ref. 19
	4sp	0.308		4sp	0.314      0.312
	5sp	0.113		5sp	0.115      0.108
	3d	-		3d	0.46      0.40

TABLE III. Final results for AgCl and AuCl. Energies are given in Hartree.

		HF	CCSD	CCSD(T)	exp.
AgCl					
	$E_{coh}$	0.1421	0.1885	0.1997	0.2031 <sup>28</sup>
	$E_{lat}$	0.2801	0.3315	0.3414	0.3487
	$a$	6.00 Å	5.57 Å	5.52 Å	5.51 Å <sup>20</sup>
	B	23 GPa	47 GPa	50 GPa	53.5 ± 0.5 GPa <sup>20</sup>
AuCl (cubic structure)					
	$E_{coh}$	0.0994	0.1730	0.1936	-
	$E_{lat}$	0.2865	0.3738	0.3956	-
	$a$	6.04 Å	5.35 Å	5.22 Å	-
AuCl (exp. structure)					
	$E_{coh}$	0.0986	0.2067	0.2328	0.1989 <sup>28</sup>
	$E_{lat}$	0.2858	0.4076	0.4348	0.4051
	$a/c$	exp. +5.8 %	exp. -3.1 %	exp. -3.9 %	6.734 Å/ 8.674 Å <sup>6</sup>

TABLE IV. Local correlation-energy increments (in Hartree) for cubic AgCl. The increments include weight factors appropriate to one formula unit of the crystal. Position vectors (i,j,k) are given in units of  $a/2$ , where  $a$  is the lattice constant.

	weight factor	lattice constant			
		5.55 Å		6.00 Å	
		CCSD	CCSD(T)	CCSD	CCSD(T)
embedded $\text{Cl}^-$	1	-0.219821	-0.228511	-0.220706	-0.229654
free $\text{Cl}^-$	-1	+0.222073	+0.231560	+0.222073	+0.231560
embedded $\text{Ag}^+$	1	-0.344594	-0.357267	-0.344572	-0.357224
free $\text{Ag}^+$	-1	+0.344551	+0.357182	+0.344551	+0.357182
$\text{Cl}(0,0,0)\text{-Cl}(0,1,1)$	6	-0.010217	-0.012170	-0.006733	-0.008127
$\text{Cl}(0,0,0)\text{-Cl}(2,0,0)$	3	-0.000455	-0.000546	-0.000299	-0.000362
$\text{Cl}(0,0,0)\text{-Cl}(2,1,1)$	12	-0.000482	-0.000580	-0.000324	-0.000393
$\text{Ag}(0,0,0)\text{-Cl}(1,0,0)$	6	-0.048464	-0.056076	-0.032905	-0.038437
$\text{Ag}(0,0,0)\text{-Cl}(1,1,1)$	8	-0.001714	-0.002040	-0.001033	-0.001234
$\text{Ag}(0,0,0)\text{-Cl}(2,1,0)$	24	-0.000899	-0.001069	-0.000566	-0.000675
$\text{Ag}(0,0,0)\text{-Ag}(0,1,1)$	6	-0.002565	-0.003000	-0.001475	-0.001724
one-body-contribution to lattice energy		+0.002209	+0.002964	+0.001346	+0.001864
two-body-contribution to lattice energy		-0.064769	-0.075481	-0.043335	-0.050952
total correlation contribution to lattice energy <sup>a</sup>		-0.062587	-0.072517	-0.041989	-0.049088

<sup>a</sup> We calculated two examples for three-body increments at 5.55 Å: The increment  $\text{Cl}(1,0,0)\text{-Cl}(0,1,0)\text{-Cl}(0,0,1)$  is +0.000041 H, at the CCSD level (CCSD(T): +0.000043); the CCSD increment for  $\text{Ag}(0,1,0)\text{-Cl}(0,0,0)\text{-Cl}(0,1,1)$  is +0.000103 H (CCSD(T): +0.000071 H). When taken from the latter cluster, CCSD results for one- and two-body increments are:  $\text{Ag}^+$ : -0.344138 H,  $\text{Cl}^-$ : -0.219889 H,  $\text{Ag-Cl}$ : -0.048006 H,  $\text{Cl-Cl}$ : -0.011010 H; comparison with the corresponding values of the Table shows that the transferability of the increments is good.



TABLE V. Local correlation-energy increments (in Hartree) for cubic AuCl. The increments include weight factors appropriate to one formula unit of the crystal. Position vectors (i,j,k) are given in units of  $a/2$ , where  $a$  is the lattice constant.

	weight factor	lattice constant			
		5.35 Å	5.35 Å	6.00 Å	6.00 Å
		CCSD	CCSD(T)	CCSD	CCSD(T)
embedded $\text{Cl}^-$	1	-0.216956	-0.225227	-0.218147	-0.226611
free $\text{Cl}^-$	-1	+0.222073	+0.231560	+0.222073	+0.231560
embedded $\text{Au}^+$	1	-0.316662	-0.329529	-0.316643	-0.329463
free $\text{Au}^+$	-1	+0.316628	+0.329420	+0.316628	+0.329420
$\text{Cl}(0,0,0)\text{-Cl}(0,1,1)$	6	-0.016820	-0.020159	-0.007916	-0.009572
$\text{Cl}(0,0,0)\text{-Cl}(2,0,0)$	3	-0.001359	-0.001604	-0.000460	-0.000549
$\text{Cl}(0,0,0)\text{-Cl}(2,1,1)$	12	-0.000697	-0.000849	-0.000302	-0.000365
$\text{Au}(0,0,0)\text{-Cl}(1,0,0)$	6	-0.094949	-0.110352	-0.053367	-0.062973
$\text{Au}(0,0,0)\text{-Cl}(1,1,1)$	8	-0.003991	-0.004798	-0.001517	-0.001818
$\text{Au}(0,0,0)\text{-Cl}(2,1,0)$	24	-0.001851	-0.002220	-0.000767	-0.000916
$\text{Au}(0,0,0)\text{-Au}(0,1,1)$	6	-0.006699	-0.007879	-0.002897	-0.003404
one-body-contribution to lattice energy		+0.005083	+0.006224	+0.003911	+0.004906
two-body-contribution to lattice energy		-0.126366	-0.147861	-0.067224	-0.079597
total correlation contribution to lattice energy <sup>a</sup>		-0.121283	-0.141637	-0.063313	-0.074691

<sup>a</sup> One three-body increment was calculated at 5.55 Å: the CCSD contribution for  $\text{Au}(0,1,0)\text{-Cl}(0,0,0)\text{-Cl}(0,1,1)$  is +0.000233 H (CCSD(T): +0.000172 H). CCSD results for one- and two-body increments, when taken from this cluster, are:  $\text{Au}^+$ : -0.315803 (-0.316652) H,  $\text{Cl}^-$ : -0.217860 (-0.217040) H,  $\text{Au-Cl}$ : -0.075516 (-0.079530) H,  $\text{Cl-Cl}$ : -0.015054 (-0.013038 H). Comparison with the numbers in parentheses, which correspond to results from clusters with one or two explicitly described ions, shows again that the transferability is good.

TABLE VI. Local correlation-energy increments (in Hartree) for AuCl (experimental structure).  $\vec{a}_{exp}$  represents the experimental lattice constants  $a=6.734$  Å and  $c=8.674$  Å. The increments include weight factors appropriate to one formula unit of the crystal.

	weight factor	lattice constant			
		$0.95*\vec{a}_{exp}$		$1.00*\vec{a}_{exp}$	
		CCSD	CCSD(T)	CCSD	CCSD(T)
embedded Cl <sup>-</sup>	1	-0.219282	-0.228022	-0.221509	-0.230664
free Cl <sup>-</sup>	-1	+0.222073	+0.231560	+0.222073	+0.231560
embedded Au <sup>+</sup>	1	-0.318164	-0.331708	-0.318760	-0.332342
free Au <sup>+</sup>	-1	+0.316628	+0.329420	+0.316628	+0.329420
Cl(0,0.25,0.19)-Cl(0,0.25,0.56)	1/2	-0.002949	-0.003472	-0.002257	-0.002678
Cl(0,0.25,0.19)-Cl(0.5,0.25,0.31)	1	-0.004004	-0.004782	-0.003016	-0.003627
Cl(0,0.25,0.19)-Cl(0.5,0.25,-0.06)	2	-0.006536	-0.008034	-0.004654	-0.005802
Cl(0,0.25,0.19)-Cl(0,0.75,-0.19)	1	-0.004097	-0.004923	-0.002514	-0.003070
Cl(0,0.25,0.19)-Cl(0.5,0.75,0.06)	2	-0.003042	-0.003814	-0.002000	-0.002556
Cl(0,0.25,0.19)-Cl(0,0.25,-0.44)	1/2	-0.000731	-0.000950	-0.000451	-0.000596
Au(0,0,0)-Cl(0,0.25,0.19)	2	-0.080882	-0.092820	-0.070456	-0.081532
Au(0,0,0)-Cl(0.5,0.25,-0.06)	4	-0.022088	-0.027312	-0.016036	-0.020052
Au(0,0,0)-Cl(0,0.25,-0.44)	2	-0.010300	-0.012722	-0.007608	-0.009576
Au(0,0,0)-Cl(0.5,0.25,0.31)	4	-0.002424	-0.002952	-0.001676	-0.002044
Au(0,0,0)-Cl(0,0.25,0.56)	2	-0.000482	-0.000578	-0.000342	-0.000410
Au(0,0,0)-Au(0.25,0.25,-0.25)	2	-0.014226	-0.017044	-0.009960	-0.011908
Au(0,0,0)-Au(0,0.5,0)	1	-0.004624	-0.005527	-0.003183	-0.003799
Cl(0,0.25,0.19)-Au(0,0.5,0)-Cl(0,0.75,-0.19) <sup>a</sup>	1	+0.001329	+0.001231	+0.001133	+0.001075
one-body-contribution to lattice energy		+0.001255	+0.001250	-0.001568	-0.002026
two-body-contribution to lattice energy		-0.156385	-0.184930	-0.124153	-0.147650
total correlation contribution to lattice energy		-0.153801	-0.182449	-0.124588	-0.148601

<sup>a</sup> Following CCSD results for one- and two-body increments have been extracted from the above three-atom cluster at  $1.00*\vec{a}_{exp}$ : Cl: -0.220213 H, Au: -0.316332 H, Cl(0,0.25,0.19)-Cl(0,0.75,-0.19): -0.003499 H, Au(0,0,0)-Cl(0,0.25,0.19): -0.061924 H. Comparison with the corresponding values of the Table shows that the transferability is less good than in the cubic structure, especially for the Au-Cl increment between next neighbors which makes the most important contribution to the lattice energy.

TABLE VII.  $C_6$  coefficients, determined from CCSD two-body increments. In-crystal polarizabilities ( $\alpha$ ) and ionization potentials (IP) were calculated as in Ref. 14. The last column is a comparison with an estimate from London's formula. All quantities except for lattice constants are in atomic units.

System	lattice constant $a$ in Å	$\Delta E$	$-C_6 = \Delta E \times r^6$	$IP_{cat}$	$IP_{an}$	$\alpha_{cat}$	$\alpha_{an}$	$-\frac{2}{3} \frac{r^6}{\alpha_1 \alpha_2} \frac{IP_1 + IP_2}{IP_1 IP_2} \times \Delta E$
Ag-Cl (AgCl)	5.55	-0.008077	170	0.46	0.44	9.3	21.5	2.5
Ag-Ag (AgCl)		-0.000428	71					2.4
Cl-Cl (AgCl)		-0.001703	283					1.9
Au-Cl (AuCl)	5.35	-0.015825	264	0.42	0.36	13.4	20.5	3.3
Au-Au (AuCl)		-0.001117	149					2.6
Cl-Cl (AuCl)		-0.002803	374					3.3